

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 05-117064

(43)Date of publication of application : 14.05.1993

(51)Int.Cl.

C04B 41/87
F01D 5/28

(21)Application number : 04-043576

(71)Applicant : TOKYO ELECTRIC POWER CO
INC:THE
NGK INSULATORS LTD

(22)Date of filing : 28.02.1992

(72)Inventor : FURUSE YUTAKA
ENDO YASUYUKI
KOBAYASHI HIROMICHI
SAKAI HIROAKI
OOI HIROYUKI

(30)Priority

Priority number : 03104722 Priority date : 09.04.1991 Priority country : JP

(54) BLADE FOR GAS TURBINE AND ITS PRODUCTION

(57)Abstract:

PURPOSE: To provide a blade used for a gas turbine and improved in the oxidation resistance and corrosion resistance.

CONSTITUTION: The coating layer of an oxide excellent in the high temperature strength and heat resistance is formed on the surface of the silicon nitride sintered member of a blade for a gas turbine. The oxide comprises one kind or more among alumina, mullite, zirconia, yttria and zircon. The coating layer of the oxide is formed in a thin film-like shape on the surface of the silicon nitride sintered member by spraying the plasma of the oxide.



⑪ Publication number : **0 508 731 A2**

⑫

EUROPEAN PATENT APPLICATION

⑳ Application number : **92303083.7**

㉑ Int. Cl.⁶ : **C04B 41/87, F01D 5/28**

㉒ Date of filing : **08.04.92**

㉓ Priority : **09.04.91 JP 104722/91**
28.02.92 JP 43576/92

㉔ Date of publication of application :
14.10.92 Bulletin 92/42

㉕ Designated Contracting States :
DE FR SE

㉖ Applicant : **THE TOKYO ELECTRIC POWER**
CO., INC.
1-3, 1-chome, Uchisaiwai-cho
Chiyoda-ku, Tokyo 100 (JP)

㉗ Applicant : **NGK INSULATORS, LTD.**
2-56 Suda-cho, Mizuho-ku
Nagoya 467 (JP)

㉘ Inventor : **Furuse, Yutaka, c/o The Tokyo Elec.**
Power Co. Inc.
1-3 Uchisaiwai-cho 1-chome, Chiyoda-ku
Tokyo 100 (JP)

Inventor : **Endo, Yasuyuki, c/o The Tokyo Elec.**
Power Co. Inc.
1-3 Uchisaiwai-cho 1-chome, Chiyoda-ku
Tokyo 100 (JP)

Inventor : **Kobayashi, Hiromichi**
11-1, Ukihashi 1-chome
Yokkaichi-shi, Mie-ken 510 (JP)

Inventor : **Sakai, Hiroaki**
54-3, Kamatsuka-cho 1-chome, Mizuho-ku
Nagoya 467 (JP)

Inventor : **Ohi, Hiroyuki**
51, Marushin-cho, Kita-ku
Nagoya 462 (JP)

㉙ Representative : **Stoner, Gerard Patrick et al**
Mewburn Ellis 2 Cursitor Street
London EC4A 1BQ (GB)

㉚ **Gas turbine blades and their production.**

㉛ A gas turbine blade improved in terms of resistance to oxidation and corrosion is provided. A coat of an oxide excelling in high-temperature strength and heat resistance is formed onto the surface of a silicon nitride sintered part forming a gas turbine blade body. At least one oxide selected from the group consisting of alumina, mullite, zirconia, yttria and zircon is used as the oxide. The oxide coat is formed on the surface of the silicon nitride-based sintered part in the form of a thin film by plasma spray coating.

The present invention relates to gas turbine blades and methods of making them.

As well known in the art, gas turbine blades required to have high mechanical properties under high-temperature and severe conditions are formed of ceramic materials such as silicon nitride and silicon carbide. One of ceramic materials having good heat resistance is a sintered silicon nitride material having a zirconia layer coated onto it, as typically set forth in JP-A-62/72582.

However, even gas turbine blades built up of such sintered silicon nitride or carbide materials of high heat resistance decrease in thickness as they are used, because they are exposed to a high-speed combustion gas flow so that they are oxidized, corroded or otherwise deteriorated at high temperatures.

A problem of particular significance associated with materials used for gas turbine blades exposed to the high-speed combustion gas flow is therefore to achieve good resistance to oxidation and hence good durability.

The present inventors have been able to achieve good resistance to oxidation and corrosion by applying an oxide coat onto the surface of a nonoxide ceramic material having excellent high-temperature strength and heat resistance.

Accordingly in one aspect of this invention, there is provided a gas turbine blade characterized in that an oxide thin film is formed on the surface of a silicon nitride-based sintered part forming a gas turbine blade member.

At least one oxide selected from alumina, mullite, zirconia, yttria and zircon may be used as said oxide.

The thin film of oxide may be coated onto the surface of said silicon nitride-based sintered part by plasma spray coating.

According to a further aspect of this invention, there is provided a method of production of a gas turbine blade characterized by comprising the steps of treating mechanically, thermally or chemically the surface of a silicon nitride-based sintered part to a surface roughness of $1.5\mu\text{m}$ or more as expressed in terms of ten-point average roughness (R_z) or $0.2\mu\text{m}$ or more as expressed in terms of center-line average roughness (R_a) and coating the surface of said part with at least one oxide selected from the group consisting alumina, mullite, zirconia, yttria and zircon by plasma spray coating.

A gas turbine blade embodying these concepts is thus obtainable by using as a part silicon nitride or a silicon nitride composite material reinforced by dispersing, e.g., silicon carbide particles or whiskers throughout it and coating the surface of the part with at least one oxide selected from the group consisting of alumina, mullite, zirconia, yttria and zircon. Preferably, the oxide coat should have a thickness of $100\mu\text{m}$ or less. One reason is that because silicon nitride or a silicon carbide dispersion-reinforced silicon nitride composite material is different from the oxide layer in terms of the rate of thermal expansion, the oxide coat is liable to peel away or crack due to repeated heating and cooling, if it is too thick. Another reason is that even at a thickness of the order of $100\mu\text{m}$ or less, the oxide coat is found to be well enough to improve the resistance of a gas turbine blade to oxidation and corrosion.

How to produce rotor blade and nozzle vane for gas turbines will now be explained.

The rotor blade or nozzle vane body for a gas turbine may be formed of either silicon nitride or a silicon carbide dispersion-reinforced silicon nitride composite material. In general, this body has an as sintered or machined surface, which must be roughened or otherwise treated to increase its bond strength or its reactivity with respect to an oxide layer to be baked or spray-coated onto it. Usable to this end are polishing with abrasive particles, oxidation by heating in the air and etching with hydrofluoric acid or other acids. Roughening or otherwise treating the part to increase its surface reactivity may be done with the best technique that is mainly determined by what material forms that part. According to our determination it is preferred that the surface roughness of the part be at least $1.5\mu\text{m}$ as expressed in terms of ten-point average roughness - R_z or at least $0.2\mu\text{m}$ as expressed in terms of center-line average roughness - R_a , both being measured according to JIS B 0601. This is because when the part has a ten-point average roughness R_z of at least $1.5\mu\text{m}$ or a center-line average roughness R_a of at least $0.2\mu\text{m}$, as measured according to JIS B0601, it comes into intimate contact with the oxide.

The oxide or oxides to be formed on the surface of the part may be selected from alumina, mullite, zirconia, yttria and zircon, and may be provided in the form of a single or multi-layer as well. In order to prevent the oxide coat from peeling away or cracking due to a thermal expansion difference between the oxide and the part, it is desirable to have provided between them an intermediate layer having its rate of thermal expansion lying halfway between the rates of thermal expansion of them.

Preferably, the oxide should be formed on the surface of the part by plasma spray coating, but this may be achieved by coating an oxide slurry onto the part; dipping the part in the oxide; forming an oxide layer on the part by spraying, followed by firing and baking; coating a mixture of a certain metal element with its oxide onto the part or dipping the latter in the former, followed by lamination by spraying, reaction and sintering; and so on.

In this way we find that it is possible to achieve excellent high temperature mechanical properties such as

creep resistance, as well as good resistance to oxidation and corrosion at high temperature.

We also find that it is possible to produce a gas turbine blade in which the oxide coat adheres well to the part and which has a high heat-resistance cycle property.

More specifically but not exclusively, this invention will now be explained with reference to the following examples.

Example 1

Provided were a sintered silicon nitride body containing Y_2O_3 and Yb_2O_3 as additives and a sintered composite part composed of a Y_2O_3 and Yb_2O_3 -containing silicon nitride material matrix and containing silicon carbide particles or whiskers as a reinforcing material. These parts were each cut to a 4-mm wide, 3-mm high and 40-mm long test piece, which was C-machined all over the surface and then oxidized at 1400°C for 100 hours in the air to form an oxide layer on the surface, to which plasma spray coating was to be applied. Each of the spray coating materials referred to in Table 1 was applied to the entire surface of the test piece at varying thicknesses of 50-100 μ m by plasma spray coating.

Oxidation and corrosion testings were done. The oxidation testing was carried out at 1400°C for 100 hours in the air according to JIS R 1609 - the oxidation resistance testing procedure for a nonoxide type of fine ceramics.

The corrosion testing was done with a high-speed combustion gas burner; that is, the sample was exposed to the gas burner using light oil as fuel at a pressure of 1 ata, a gas flow rate of 200m/sec. and a temperature of 1400°C for 10 hours. The degree of corrosion was estimated by profiling the sample surface with a surface roughness meter before and after the exposure testing. The results of the oxidation and corrosion testings are shown in Tables 1 and 2.

Table 1

	Substrate	Spray Coating Material	Weight Increase by Oxidation in mg/cm ²
5	Example 1	SN Alumina	0
	Example 2	SN Mullite	0
10	Example 3	SN Zirconia	0
	Example 4	SN Yttria	0
	Example 5	SN Zircon	0
15	Example 6	C Alumina	0
	Example 7	C Mullite	0
20	Example 8	C Zirconia	0
	Example 9	C Yttria	0
	Example 10	C Zircon	0
25	Comparative Example 1	SN -	0.5
30	Comparative Example 2	C -	0.3

35 Note that "SN" and "C" stand for silicon nitride
and composite material, respectively, and that the weight
increase by oxidation is given by the average value of
three measurements.

40

45

50

55

Table 2

	Substrate	Spray Coating Material	Thickness Decrease in μm
5	Example 1	SN Alumina	0
	Example 2	SN Mullite	0
10	Example 3	SN Zirconia	0
	Example 4	SN Yttria	0
	Example 5	SN Zircon	0
15	Example 6	C Alumina	0
	Example 7	C Mullite	0
20	Example 8	C Zirconia	0
	Example 9	C Yttria	0
	Example 10	C Zircon	0
25	Comparative Example 1	SN	5
30	Comparative Example 2	C	6

Note that the thickness decrease is given by the average value of three measurements.

Example 2

Formed of silicon nitride were a number of test pieces which were investigated as to their surface roughness and their adhesion to oxide coats. The results are set out in Table 3. The test pieces of Examples 21-25 were heat-treated at 1400°C for 10 hours in the air after machining, and the test pieces of Examples 26-30 were sand-blasted with 50% by weight of #36 silicon carbide grit and 50% by weight of #36 alumina grit. In Comparative Examples 11-15 the test pieces were mechanically processed on their as-sintered surfaces with a #140 grinder, and in Comparative Examples 16-20 the test pieces were heat-treated at 1300°C for 1 hour in the air after processing.

By plasma spray coating, these test pieces were coated with about 100- μm thick coats of oxides, say, alumina, mullite, zirconia, yttria and zircon to obtain samples. The adhesion of the oxide coats to the surfaces of the test pieces and the heat-resistant cycle characteristics of the samples, when they were repeatedly subjected to a heating/cooling cycle at between room temperature and 1400°C, were measured for estimation. The results are shown in Table 3, as already mentioned.

Table 3

		Surface Roughness in μm		Spray Coating Material	A	B
		Rz	Ra			
5	Example 21	1.7	0.2	Alumina	Good	Good
	Example 22	1.7	0.2	Mullite	Good	Good
10	Example 23	1.7	0.2	Zirconia	Good	Good
	Example 24	1.7	0.2	Yttria	Good	Good
15	Example 25	1.7	0.2	Zircon	Good	Good
	Example 21	12.0	2.2	Alumina	Good	Good
	Example 22	12.0	2.2	Mullite	Good	Good
20	Example 23	12.0	2.2	Zirconia	Good	Good
	Example 24	12.0	2.2	Yttria	Good	Good
25	Example 25	12.0	2.2	Zircon	Good	Good
	Comparative Example 11	0.7	0.1	Alumina	Bad	-
30	Comparative Example 12	0.7	0.1	Mullite	Bad	-
	Comparative Example 13	0.7	0.1	Zirconia	Bad	-

	Comparative Example 14				
	0.7	0.1	Yttria	Bad	-
5	Comparative Example 15				
	0.7	0.1	Zircon	Bad	-
	Comparative Example 16				
	1.1	0.1	Alumina	Good	Bad*
10	Comparative Example 17				
	1.1	0.1	Mullite	Good	Bad*
	Comparative Example 18				
15	1.1	0.1	Zirconia	Good	Bad*
	Comparative Example 19				
	1.1	0.1	Yttria	Good	Bad*
20	Comparative Example 20				
	1.1	0.1	Zircon	Good	Bad*

A: Adhesion of the coats to the test pieces

25 B: Adhesion of the coats when the samples were repeatedly subjected to a heating/cooling cycle.

30 *: Peeling

35 The adhesion of the oxide coats was estimated by visually observing whether or not they were uniformly coated onto the surfaces of the test pieces. As can be understood from Table 3, the oxide coats adhered well to the test pieces in Examples 21-30 and Comparative Examples 16-20, but the oxide coats adhered only locally to the test pieces with the rest peeling away.

40 Estimating the adhesion of the oxide coats to the test pieces was made by subjecting the samples repeatedly to a heating/cooling cycle at between room temperature and 1400°C and observing the test piece/oxide coat interfaces under an optical microscope per cycle. In Examples 21-30 no peeling was observed even after the samples had been subjected to 200 heating/cooling cycles at between room temperature and 1400°C, but in Comparative Examples 16-20 peeling occurred by one such a heating/cooling cycle.

45 As can be understood from what has been described above, the gas turbine blade can be made which excels in surface resistance to oxidation and corrosion and so can be used without suffering any thickness decrease over extended periods of time even under high-temperature and severe conditions. According to the methods described herein; it is possible to produce a gas turbine blade which can well stand up to use at high temperatures, and which is good in terms of the adhesion of the oxide coat to the blade body and heat-resistance cycle characteristics.

Claims

- 50
1. A gas turbine blade comprising an oxide thin film coated on the surface of a blade body formed of a silicon nitride-based sintered part.
 2. A gas turbine blade as claimed in claim 1, wherein at least one oxide selected from alumina, mullite, zirconia, yttria and zircon is used as said oxide.
 3. A gas turbine blade of claim 1 or 2 wherein said oxide is coated onto the surface of said blade body in the form of a thin film by plasma spray coating.
- 55

4. A method of making a gas turbine blade comprising forming an oxide thin film on the surface of a silicon nitride-based sintered blade body.

5. A method according to claim 4 comprising the steps of:

5 treating mechanically, thermally or chemically the surface of a silicon nitride-based sintered part, to a surface roughness of at least $1.5\mu\text{m}$ or more as expressed in terms of ten-point average roughness (R_z), or a surface roughness of at least $0.2\mu\text{m}$ or more as expressed in terms of centre-line average roughness (R_a), and

10 plasma-spraying at least one of alumina, mullite, zirconia, yttria and zircon onto the surface of said sintered part.

15

20

25

30

35

40

45

50

55